

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in Polymer Production

We, CELANESE CORPORATION OF AMERICA, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in the production of oxymethylene polymers and is an improvement in or modification of the invention described in co-pending Application No. 11839/62 (Serial No. 974,819) filed 28th March 1962.

In our Application No. 11839/62 (Serial No. 974,819) there is described a process for producing an oxymethylene polymer directly in powder form by carrying out the polymerisation of trioxane, or its copolymerisation with another monomer, in a liquid mixture containing at least 50 weight percent of trioxane while subjecting the polymerising material simultaneously to shearing and blending, the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet progressed to the same degree, and continuing the shearing and blending until a product is obtained in which at least 65 weight percent of the trioxane present is in polymer form.

By operating in this way the polymer can be obtained as a powder without the necessity of grinding the hard lump of polymer which is commonly formed when using a highly efficient catalyst such as boron fluoride unless an inconveniently large amount of liquid diluent is present. In the process it is, however, advantageous to have

present a small amount of diluent as this aids in achieving an effective shearing, mixing and forwarding action in apparatus of the type described.

It has now been found that effective operation can be achieved when liquid trioxane is present throughout the process to a larger extent than is the case when conversion reaches or exceeds 65 percent of the trioxane initially present and a powdered product obtained, mixed with unconverted trioxane, under conditions which in the absence of the shearing and blending, lead to the formation of a solid lump of powder, a result which can occur even with conversions of little more than 25 percent of the trioxane initially present.

According to the invention, therefore, an oxymethylene polymer is obtained directly in powder form by a process in which trioxane is polymerised or copolymerised with another monomer in a liquid mixture containing at least 50 weight percent of trioxane while subjecting the polymerising material simultaneously to shearing and blending; the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet progressed to the same degree, the process being characterised by the fact that throughout the operation an excess of liquid trioxane above that left after 65 weight percent conversion is maintained in admixture with the forming polymer and is thereafter separated from the powdered polymer obtained.

The recovered trioxane can be directly recycled to the polymerisation so that no material loss occurs while, in view of the low temperature at which the polymerisation can be carried out, the heat loss is negligible and completely outweighed by

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the advantage achieved by operating with a relatively short shearing and blending time for a given feed of trioxane.

The process can be carried out satisfactorily in the apparatus described in Application No. 11839/62 (Serial No. 974,819) and using conditions differing from those in that Application only by the maintenance of a suitable excess of liquid trioxane throughout the shearing and blending.

The following Example illustrates the invention:—

Example

Trioxane was copolymerised with 3.2 percent of its weight of ethylene oxide in the apparatus described in Application No. 11839/62 (Serial No. 974,819), the catalyst being 50 parts of boron fluoride dibutyl etherate per million parts of the mixture. The polymerisation mixture contained 5 parts by weight of cyclohexane per 100 parts of trioxane and the mixture was fed through at different rates so as to obtain products containing polymer representing approximately 27 percent and 31 percent conversion of the total trioxane fed. In both cases the product was a slurry of powdered polymer from which the excess trioxane could easily be separated to yield a dry powder. The trials were repeated using a monomer mixture containing 3.4 percent by weight of ethylene oxide based on the trioxane, the rates of passage through the polymeriser being such as to yield products containing polymer representing approximately 29 percent and 31 percent conversions of the total trioxane fed. Again, the products were slurries of powdered polymer from which the excess trioxane could easily be separated to give a dry powder.

In contrast to the results obtained in the above Example, four trials carried out

under similar conditions but without shearing and mixing with the polymerisation being stopped at the same conversions each yielded a solid polymer mass.

Other trials carried out under the conditions of the invention have been conducted using longer shearing and blending periods and powdered polymer has been similarly obtained in slurry form at the higher conversions thus permitted, for instance conversions of 40 to 45 percent.

WHAT WE CLAIM IS:—

1. Process for the production of an oxymethylene polymer directly in powder form by polymerising trioxane or copolymerising trioxane with another monomer in a liquid mixture containing at least 50 weight percent of trioxane while subjecting the polymerising material simultaneously to shearing and blending, the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet progressed to the same degree, the process being characterised by the fact that throughout the operation an excess of liquid trioxane above that left after 65 weight percent conversion is maintained in admixture with the forming polymer and is thereafter separated from the powdered polymer obtained.

2. Process for the production of an ethylene oxide-trioxane copolymer, substantially as described in the Example.

3. Ethylene oxide-trioxane copolymers and other oxymethylene polymers whenever produced by the process claimed in Claim 1 or Claim 2.

A. J. BUTTERWORTH,
Chartered Patent Agent, RA
49 Old Bond Street,
London, W.1.

J. A. Butterworth

the advantage achieved by operating with a relatively short shearing and blending time for a given feed of trioxane.

- 5 The process can be carried out satisfactorily in the apparatus described in Application No. 11839/62 (Serial No. 974,819) and using conditions differing from those in that Application only by the maintenance of a suitable excess of liquid trioxane
10 throughout the shearing and blending.

The following Example illustrates the invention:—

Example

- 15 Trioxane was copolymerised with 3.2 per cent of its weight of ethylene oxide in the apparatus described in Application No. 11839/62 (Serial No. 974,819), the catalyst being 50 parts of boron fluoride dibutyl etherate per million parts of the mixture.
20 The polymerisation mixture contained 5 parts by weight of cyclohexane per 100 parts of trioxane and the mixture was fed through at different rates so as to obtain products containing polymer representing approximately 27 percent and 31 percent conversion of the total trioxane fed. In both cases
25 the product was a slurry of powdered polymer from which the excess trioxane could easily be separated to yield a dry powder.
30 The trials were repeated using a monomer mixture containing 3.4 percent by weight of ethylene oxide based on the trioxane, the rates of passage through the polymeriser being such as to yield products
35 containing polymer representing approximately 29 percent and 31 percent conversions of the total trioxane fed. Again, the products were slurries of powdered polymer from which the excess trioxane could
40 easily be separated to give a dry powder.

In contrast to the results obtained in the above Example, four trials carried out

under similar conditions but without shearing and mixing with the polymerisation being stopped at the same conversions each
45 yielded a solid polymer mass.

Other trials carried out under the conditions of the invention have been conducted using longer shearing and blending periods and powdered polymer has been similarly
50 obtained in slurry form at the higher conversions thus permitted, for instance conversions of 40 to 45 percent.

WHAT WE CLAIM IS:—

1. Process for the production of an oxy-
55 methylene polymer directly in powder form by polymerising trioxane or copolymerising trioxane with another monomer in a liquid mixture containing at least 50 weight percent of trioxane while subjecting the poly-
60 merising material simultaneously to shearing and blending, the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet pro-
65 gressed to the same degree, the process being characterised by the fact that throughout the operation an excess of liquid trioxane above that left after 65 weight percent conversion is maintained in admixture with the form-
70 ing polymer and is thereafter separated from the powdered polymer obtained.

2. Process for the production of an ethylene oxide-trioxane copolymer, substantially
75 as described in the Example.

3. Ethylene oxide-trioxane copolymers and other oxymethylene polymers whenever produced by the process claimed in Claim 1 or Claim 2.

A. J. BUTTERWORTH,
Chartered Patent Agent, *RH*
49 Old Bond Street,
London, W.1.



J. A. Butterworth